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Standard Methods for
ASSAY OF ORGANIC PEROXIDES[1]

This Standard is issued under the fixed designation E 298; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 These methods cover the assay of organic peroxides. Two procedures are given, depending upon their ease of reduction:

1.1.1 *Sodium Iodide, Room Temperature Method*, for organic peroxides easy to reduce, and

1.1.2 *Sodium Iodide, 60 C Method*, for organic peroxides that are moderately stable.

2. Purity of Reagents

2.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[2] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

2.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specification D 1193, for Reagent Water.[3]

SODIUM IODIDE, ROOM TEMPERATURE METHOD

3. Scope

3.1 This method covers the assay of organic peroxides that are easily reduced such as hydroperoxides and diacyl peroxides. Dialkyl peroxides do not react, while peresters and bridge-type peroxides like ascaridole react slowly and incompletely.

3.2 Specific peroxides that can be analyzed by this procedure include the following:

3.2.1 *Diacyl Peroxides*—Benzoyl 2,4-dichlorobenzoyl, *p*-chlorobenzoyl, lauroyl, acetyl, and decanoyl peroxides.

3.2.2 *Dibasic Acid Peroxide*—Succinic acid peroxide.

3.2.3 *Ketone Peroxides*—Cyclohexanone peroxide and methyl ethyl ketone peroxide.

3.2.4 *Alkyl Hydroperoxides*—*t*-Butylhydroperoxide and 2,5-dimethylhexane-2,5-dihydroperoxide.

4. Summary of Method

4.1 A sample is dissolved in a mixture of methylene chloride and acetic acid. A saturated solution of sodium iodide is added and the mixture is allowed to react in the dark at room temperature for 15 min. The liberated iodine is then titrated with standard sodium thiosulfate solution.

5. Interferences

5.1 Conjugated diolefins interfere by absorbing iodine.

6. Apparatus

6.1 *Iodine Flasks*, 250-ml, with stoppers.

NOTE 1—All glassware should be thoroughly cleaned with dichromate cleaning solution before use.

7. Reagents

7.1 *Acetic Acid, Glacial.*

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[1] These methods are under the jurisdiction of ASTM Committee E-15 on Analysis and Testing of Industrial Chemicals and are the direct responsibility of Subcommittee E-15.22 on Functional Groups.

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[2] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."

[3] *1974 Annual Book of ASTM Standards*, Part 31.

7.2 *Carbon Dioxide*, cylinder.

7.3 *Methylene Chloride.*

7.4 *Sodium Iodide, Saturated Solution*—Prepare a saturated solution of sodium iodide (NaI) in de-aerated water. This solution should be prepared just prior to use and kept in a brown bottle.

7.5 *Sodium Thiosulfate, Standard Solution* (*0.1 N*)—Prepare and standardize a 0.1 *N* solution of sodium thiosulfate ($Na_2S_2O_3$) in accordance with the appropriate sections of ASTM Methods E 200, Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis.[4]

7.6 *Starch Indicator Solution*—Triturate 1 g of soluble starch with a few milliliters of cold water, and slowly pour into 100 ml of boiling water while stirring. Cool and add 0.3 g of mercuric iodide (HgI_2) as a preservative.

7.7 *Water, De-aerated*—Pass carbon dioxide (CO_2) through distilled water for several minutes prior to use.

8. Procedure

8.1 Add 20 ml of acetic acid to a 250-ml iodine flask and sparge with a rapid flow of CO_2 for 2 min. Stopper the flask and reserve for the sample.

8.2 Accurately weigh a sample containing 3 to 4 meq of active oxygen and transfer to the flask.

NOTE 2—The approximate weight of the sample to be used in the analysis may be calculated as follows:

$$\text{Sample weight, g} = 3.5M/(2C \times 1000)$$

where:

M = molecular weight of the compound, and

C = number of peroxide groups in the molecule.

Volatile liquid peroxides may be diluted to a known volume with acetic acid and aliquots taken for analysis.

8.3 Add 10 ml of methylene chloride and restopper. Swirl briefly to dissolve the sample.

8.4 Add 5 ml of freshly prepared saturated NaI solution. Restopper and swirl. Place a few milliliters of water in the well of the flask and allow to stand in the dark at room temperature for 15 min.

8.5 Add 50 ml of de-aerated water and titrate with 0.1 *N* $Na_2S_2O_3$ solution until the solution is a pale straw color. Add 1 to 2 ml of starch solution and continue the titration to the sharp disappearance of the blue color. Record the number of milliliters required for titration.

8.6 Subtract the number of milliliters required for titration of a blank carried through the entire procedure and calculate the assay value of the sample.

NOTE 3—The blank titration should normally require 0.05 ml or less of 0.1 *N* $Na_2S_2O_3$ solution. The results should be discarded and the analysis repeated if high blank values are obtained.

9. Calculation

9.1 Calculate the assay as follows:

$$\text{Assay, as percent compound} = [(A - B) \times N \times M \times 100]/(W \times 2C \times 1000)$$

where:

A = milliliters of $Na_2S_2O_3$ solution required for titration of the sample,

B = milliliters of $Na_2S_2O_3$ solution required for titration of the blank,

N = normality of the $Na_2S_2O_3$ solution,

C = number of peroxide groups in the molecule,

M = molecular weight of the compound, and

W = grams of sample used.

9.2 Calculate the percent active oxygen in the compound as follows:

$$\text{Active oxygen, percent} = [((A - B) \times N \times 0.008)/W] \times 100$$

10. Report

10.1 Report the assay value of the compound to the nearest 0.01 percent. Duplicate runs that agree within 0.03 percent are acceptable for averaging (95 percent confidence level).

11. Precision

11.1 The following criteria shall be used for judging the acceptability of results:

11.1.1 *Repeatability* (*Single Analyst*)—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.0096 percent absolute at 18 degrees of freedom. Two such values should be considered suspect (95 percent confidence level) if they differ by more than 0.03 percent absolute.

11.1.2 *Reproducibility* (*Multilaboratory*)—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.049 percent absolute at 5 degrees of freedom. Two such values should be considered suspect (95 percent confidence level) if they differ by more than 0.18 percent absolute.

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[4] *1974 Annual Book of ASTM Standards*, Part 30.

SODIUM IODIDE, 60 C METHOD

12. Scope

12.1 This method covers the assay of organic peroxides that are moderately stable, such as peresters, di-*n*-alkyl peroxides, and *n*-alkyl peroxides. These peroxides react slowly with sodium iodide at room temperature, but do not require the use of hydriodic acid.

12.2 Specific peroxides that can be analyzed by this procedure include the following: *t*-butyl peracetate, *t*-butyl peroxyisobutyrate, di-*t*-butyl dipherphthalate, *t*-butyl perbenzoate, and 2,2-*bis*(*t*-butylperoxy) butane.

13. Summary of Method

13.1 A sample is dissolved in glacial acetic acid. Saturated sodium iodide solution is then added and the mixture is allowed to react for 1 h at 60 C. The liberated iodine is titrated with standard sodium thiosulfate solution.

14. Interferences

14.1 Conjugated diolefins interfere under the conditions of analysis by absorbing iodine.

15. Apparatus

15.1 *Iodine Flasks*, 250-ml with stopper (Note 1).

15.2 *Water Bath*, maintained at 60 ± 1 C.

16. Reagents

16.1 *Acetic Acid, Glacial.*

16.2 *Carbon Dioxide*, cylinder.

16.3 *Sodium Iodide, Saturated Solution*—See 7.4.

16.4 *Sodium Thiosulfate, Standard Solution (0.1 N)*—See 7.5.

16.5 *Starch Indicator Solution*—See 7.6.

16.6 *Water, De-aerated*—See 7.7.

17. Procedure

17.1 Add 20 ml of acetic acid to a 250-ml iodine flask and sparge with a rapid flow of carbon dioxide (CO_2) for 2 min. Stopper the flask and reserve for the sample.

17.2 Accurately weigh a sample containing 3 to 4 meq of active oxygen and transfer to the flask (Note 2).

17.3 Add 5 ml of freshly prepared saturated NaI solution (Note 4). Restopper tightly and swirl. Place a few milliliters of water in the well of the flask and allow the flask to stand partially submerged in a water bath maintained at 60 C for 1 h.

NOTE 4—Some peroxides may require the addition of a small amount of hydrochloric acid (HCl) to react completely in a reasonable time. In this case 1 ml of concentrated HCl shall be added to the solution just before it is placed in the water bath.

17.4 Remove the flask from the bath and cool to room temperature.

17.5 Add 60 ml of de-aerated water and titrate with 0.1 *N* $Na_2S_2O_3$ solution until the solution is a pale straw color. Add 1 to 2 ml of starch solution and continue the titration to the sharp disappearance of the blue color. Record the number of milliliters required for titration.

17.6 Subtract the number of milliliters required for titration of a blank carried through the entire procedure and calculate the assay value of the sample.

NOTE 5—The blank titration should normally require about 0.10 ml of 0.1 *N* $Na_2S_2O_3$ solution. The results should be discarded and the analysis repeated if high blank values are obtained.

18. Calculation

18.1 Calculate the assay as follows:

Assay, as percent compound

$$= [(A - B) \times N \times M \times 100]/(W \times 2C \times 1000)$$

where:

A = milliliters of $Na_2S_2O_3$ solution required for titration of the sample,

B = milliliters of $Na_2S_2O_3$ solution required for titration of the blank,

N = normality of the $Na_2S_2O_3$ solution,

C = number of peroxide groups in the molecule,

M = molecular weight of the compound, and

W = grams of sample used.

18.2 Calculate the percent of active oxygen in the compound as follows:

Active oxygen, percent

$$= [((A - B) \times N \times 0.008)/W] \times 100$$

19. Report

19.1 Report the assay value of the compound to the nearest 0.01 percent. Duplicate runs that agree within 0.15 percent are acceptable for averaging (95 percent confidence level).

20. Precision

20.1 The following criteria shall be used for judging the acceptability of results:

20.1.1 *Repeatability (Single Analyst)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.057 percent absolute at 12 degrees of freedom. Two such values should be considered suspect (95 percent confidence level) if they differ by more than 0.17 percent absolute.

20.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.131 percent absolute at 5 degrees of freedom. Two such values should be considered suspect (95 percent confidence level) if they differ by more than 0.48 percent absolute.

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